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МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ

Ethylene for industrial use — Determination of traces of polar compounds — Preparation of condensate samples by low-temperature scrubbing technique

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*Éthylène à usage industriel — Dosage des traces de composés polaires. — Préparation
d'échantillons concentrés par piégeage cryogénique*

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Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 8916 was prepared by Technical Committee ISO/TC 47, *Chemistry*.

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Annex A of this International Standard is for information only.

Introduction

The exact determination of the polar compounds content in gaseous samples is particularly difficult for the following reason. The polar compounds of interest are liable to exhibit more or less pronounced adsorption phenomena at the solid surfaces of the sampling cylinders and of the tubes of conventional gas analytical devices.

Conventional gas analytical devices show relative errors of several hundred per cent, despite the special precautions taken during sampling.

In this case three methods of operation are generally possible:

a) The determination, using a continuous analyser with a specific in-line sensor, in a streaming sample gas flow (see ISO 8917). Even though, in this case, the waiting times for a reliable and stable signal indication may be remarkably long. This signal is obtained when the zone of equilibrium between the gaseous polar compound and its adsorption layer in the flow system has reached the exit of the measuring cell. This technique requires a specific detector, which may be an on-line gas chromatograph or a mass spectrometer. In the most severe case, that of the most polar compound (water), a large number of commercially available special sensor devices may be used (see ISO 8917). This is a very special case.

b) The preconcentration by adsorption of a given compound on an appropriate precolumn, which is degassed by heating in a specially adapted gas chromatograph. This method is well suited for routine application in series and in special cases. It is not universally applicable. The desorption itself shall be checked for every compound to be analysed. Incomplete desorption and even thermal decomposition of certain compounds, have been observed.

c) The concentration into a liquid at low temperature by a scrubbing technique. In this case also, adsorption on the glass walls of the scrubbing absorbers may occur. However, this is a concentration process into a very small liquid volume and the dimensions of these scrubbing absorbers are very small.

A universally applicable method may be used and this technique is the subject of this International Standard.

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Ethylene for industrial use — Determination of traces of polar compounds — Preparation of condensate samples by low-temperature scrubbing technique

1 Scope

This International Standard specifies a method of sampling ethylene by scrubbing at dry ice temperature (195 K).

NOTE — This method is also applicable to other gases having boiling temperatures less than 195 K (for example methane, nitrogen, oxygen, carbon monoxide, ethane).

It permits the concentration of traces of all the less volatile polar compounds (water, alcohols, esters, acids, amines, etc.) in a small amount of liquid phase practically without any interference due to adsorption phenomena on the relatively small internal surfaces of the scrubbing absorber. This sampling technique permits the exact determination of all these polar compounds at contents greater than 0,01 mg/m³ at normal temperature and pressure.

It is also applicable for the determination of hydrocarbons with a higher boiling point (for example traces of oil in ethylene).

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 7382 : 1986, *Ethylene for industrial use — Sampling in the liquid and the gaseous phase.*

3 Principle

Passage of a known volume of gaseous sample through two identical scrubbing absorbers of fritted glass in series in a cold bath and filled with a known amount of a suitable liquid, then analytical determination in these solutions can be carried out by any suitable method according to the polar compound to be determined (for example gas chromatography, acidimetric titration, Karl Fischer titration).

Application of the mathematical law for the summation of an infinite converging geometric progression to the concentrations of the compounds to be determined separately in these two absorbers as the first members of this progression.

4 Materials

4.1 Extraction solvents of recognized analytical grade, having melting temperatures less than 195 K.

Miscibility with the compounds to be determined is essential and must be verified in each case.

The following liquids may be suitable :

Table 1 — Suitable extraction solvents

| Name | Formula | Vapour pressure at 195 K Pa*) |
|------------------|-----------------------------------------------|-------------------------------|
| Acetone | (CH ₃) ₂ CO | 20 |
| Methanol | CH ₃ OH | 2,65 |
| Propan-1-ol | C ₃ H ₇ OH | 0,05 |
| Propan-2-ol | C ₃ H ₇ OH | 0,13 |
| Tetrahydrofuran | C ₄ H ₈ O | 15,5 |
| Carbon disulfide | CS ₂ | 90 |
| Dichloromethane | CH ₂ Cl ₂ | 66,5 |
| n-Hexane | C ₆ H ₁₄ | 9,3 |
| Toluene | C ₆ H ₅ CH ₃ | 0,67 |

*) 1 Pa = 10⁻⁵ bar

4.2 Cryogenic mixture: Dry ice in acetone or propan-2-ol.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Two small glass absorbers, of identical geometry, connected in series by spherical ground glass joints (see figure 1), with dimensions such that 10 ml of solvent are sufficient to immerse the fritted parts.

5.2 Dewar flask, of appropriate diameter, capable of containing the absorbers in series (5.1).

5.3 Calibrated gas meter, fitted to the outlet of the second absorber (see figure 2). This gas meter operates at atmospheric pressure.

6 Procedure

6.1 Safety measures

See ISO 7382 : 1986, 2.1 and its annex, describing an ejector to air for the removal of the sample gas after passage through the absorbers and the gas meter.

6.2 Preparation of apparatus

Connect the two absorbers (5.1) in series and fill each with an identical quantity (about 10 ml), weighed to the nearest 1 mg, of a suitable extraction solvent (4.1).

It is essential to obtain a homogeneous solution of the compound to be determined after absorption and warming of the absorbers to ambient temperature. The choice of a suitable solvent from those given in 4.1 shall be made on the basis of these considerations.

Introduce the two connected absorbers with closed stopcocks into the Dewar flask (5.2), containing the cryogenic mixture (4.2); fit the gas meter (5.3) to the outlet of the second absorber and connect it to the ejector to air (see 6.1).

6.3 Installation and setting in operation of the apparatus

Connect the apparatus, prepared as in 6.2, directly to the ethylene tank with pipes as short as possible.

If polar compounds with higher boiling points are to be determined, it is recommended that the pipes be heated. In cases of determination of polar compounds (especially water), even this is not sufficient at normal heating temperatures less than 300 °C. In this case, purging the shortest possible pipe for approximately 30 min before switching to the absorbers should be sufficient.

The use of an intermediate sample cylinder may lead to an inaccurate analysis and should be avoided.

Open the discharge valve of the tank and regulate the sample flow by means of the adjustable sampling valve, heated, if necessary, to obtain a flow rate of about 50 l/h at atmospheric pressure.

Open the stopcocks of the absorbers. Determine the exact quantity of sample gas which has flowed through the cooled absorbers, using the calibrated gas meter (5.3).

6.4 Preparation of test solutions

At the end of the sampling, close the four stopcocks and transfer to the laboratory the absorbers still in the cooling Dewar flask containing the cryogenic mixture.

In the laboratory, connect the exit of each absorber to a drying tube (calcium chloride, dried molecular sieve, etc.) to prevent the penetration of atmospheric moisture, then open the exit stopcock. Remove the Dewar flask and allow the absorbers to warm up to ambient temperature for about 15 min.

Before beginning the determination, check the original masses of solvent; however, any loss of solvent by evaporation into the sample gas flow can be excluded because of the negligibly small vapour pressure of the solvent (see 4.1). If an increase in mass has occurred, it may be due to a compound of no interest being present in a higher concentration. Take this mass into account in the subsequent calculations.

6.5 Subsequent determination

Determine separately the polar compounds of interest in each of the two solutions (6.4), either by gas chromatography or by a titrimetric method, and carry out a blank test.

7 Expression of results of analysis

The scrubbing of a condensable compound from a non-condensable gas flow is necessarily incomplete because of difficulties of diffusion in the phase boundary layer.

However, if two absorbers of identical geometry and filled with the same amount of the same scrubbing solvent are streamed through in series by the same sample gas at the same temperature, the relative absorbed ratio is proportional to the concentration of the condensable compound in the respective absorber, i.e. the concentrations of the absorbed quantities in the liquid phases are the first two terms of an infinite converging geometric progression.

These first two terms are sufficient for calculating exactly the sum of the entire infinite progression (i.e. the imaginary sum of all the concentrations in imaginary infinite absorbers in series, and together these would certainly absorb the total amount of the compound to be determined).

The fugacity of an individual compound determines the degree of convergence of the progression.

The respective sum can be calculated as follows:

$$\sum_{n=1}^{\infty} C_n = C_1 \times \frac{1 - \alpha^{\infty}}{1 - \alpha}$$

with

$$\begin{aligned} \alpha &= \frac{C_2}{C_1} \\ &= \frac{C_{n+1}}{C_n} < 1 \end{aligned}$$

For the totality of condensable compound, it follows that

$$\sum_{n=1}^{\infty} C_n = \frac{C_1^2}{C_1 - C_2}$$

The total content of the condensable compound, expressed in grams per cubic metre, at ambient temperature and pressure is given by the formula

$$\frac{1}{100 V} \times \frac{C_1^2 m_1^2}{C_1 m_1 - C_2 m_2}$$

where

V is the volume, in cubic metres, of sample gas at ambient temperature and pressure, measured by the gas meter at the exit of the second absorber;

C_1 and C_2 are the concentrations of the condensable compound expressed as a percentage by mass, determined respectively in the solution of each of the two absorbers;

m_1 and m_2 are respectively the masses, in grams, of the solution in each of the two absorbers, measured by weighing after absorption and warming up to ambient temperature.

Exemple:

With

- an analysis of the scrubbing solutions made by gas chromatography with a flame ionization detector,
- a chromatographic technique allowing a detection limit of 1 mg/kg to be attained,
- two quantities of solvent equal to 10 g,
- a volume of sample gas of 10 litres, measured at ambient temperature and pressure,

it is then possible to attain, in gaseous phase, a detection limit of 1 mg/m³ for the determination of any less volatile or polar compound. If necessary, the sample gas flow can be prolonged without impairing the accuracy of the entire analysis.

NOTE — The masses may be changed a bit during the absorption process. This has to be corrected with the additionally checked weight.

8 Test report

The test report shall include the following particulars:

- a) identification of the sample;
- b) a reference to the method used, the indication of solvent and its quantities;
- c) the results and the way in which they have been expressed;
- d) any unusual features noted during the determination;
- e) any operation not included in this International Standard or in the International Standard to which reference is made, or any operation regarded as optional.

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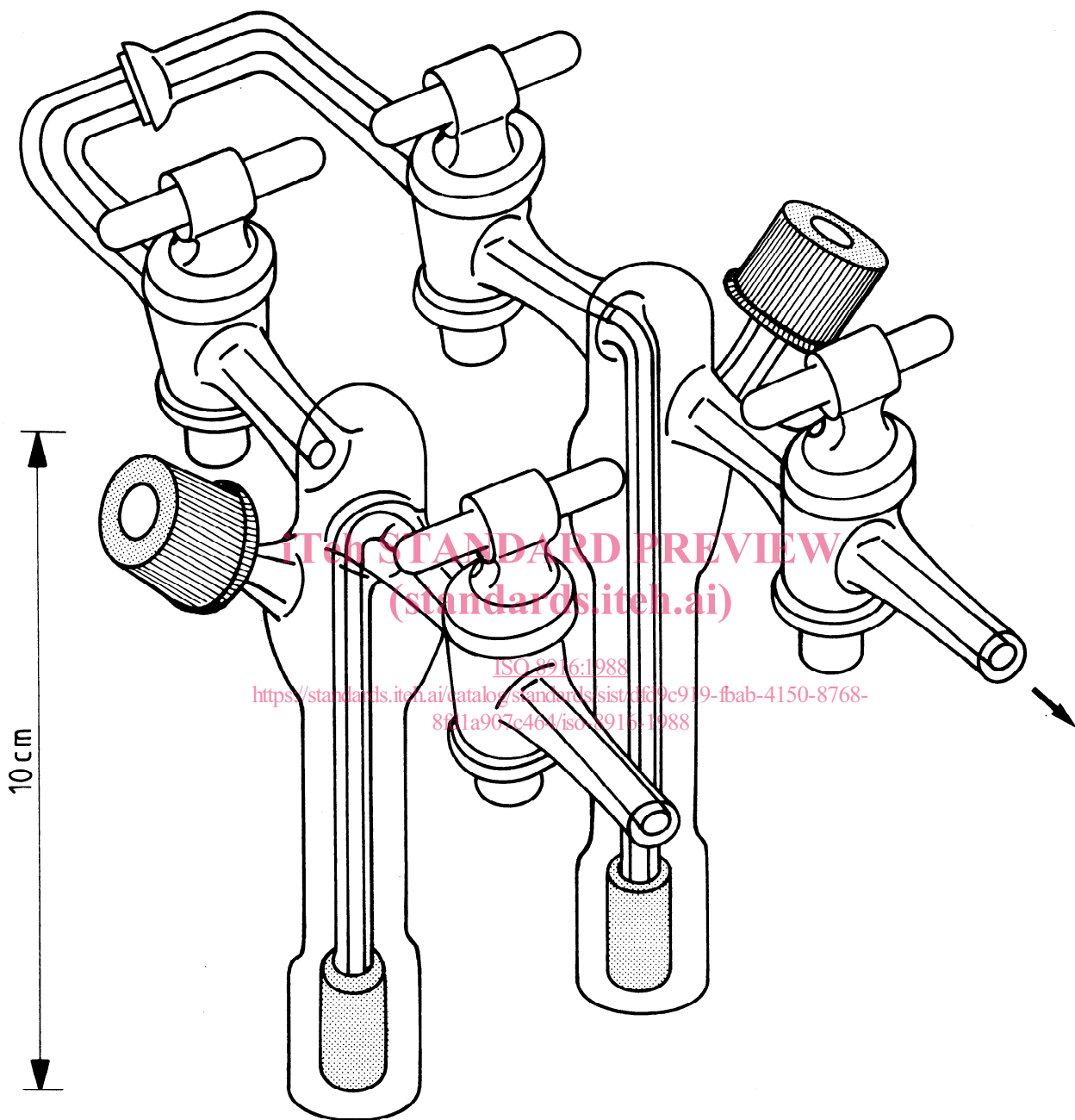


Figure 1 — Absorption apparatus

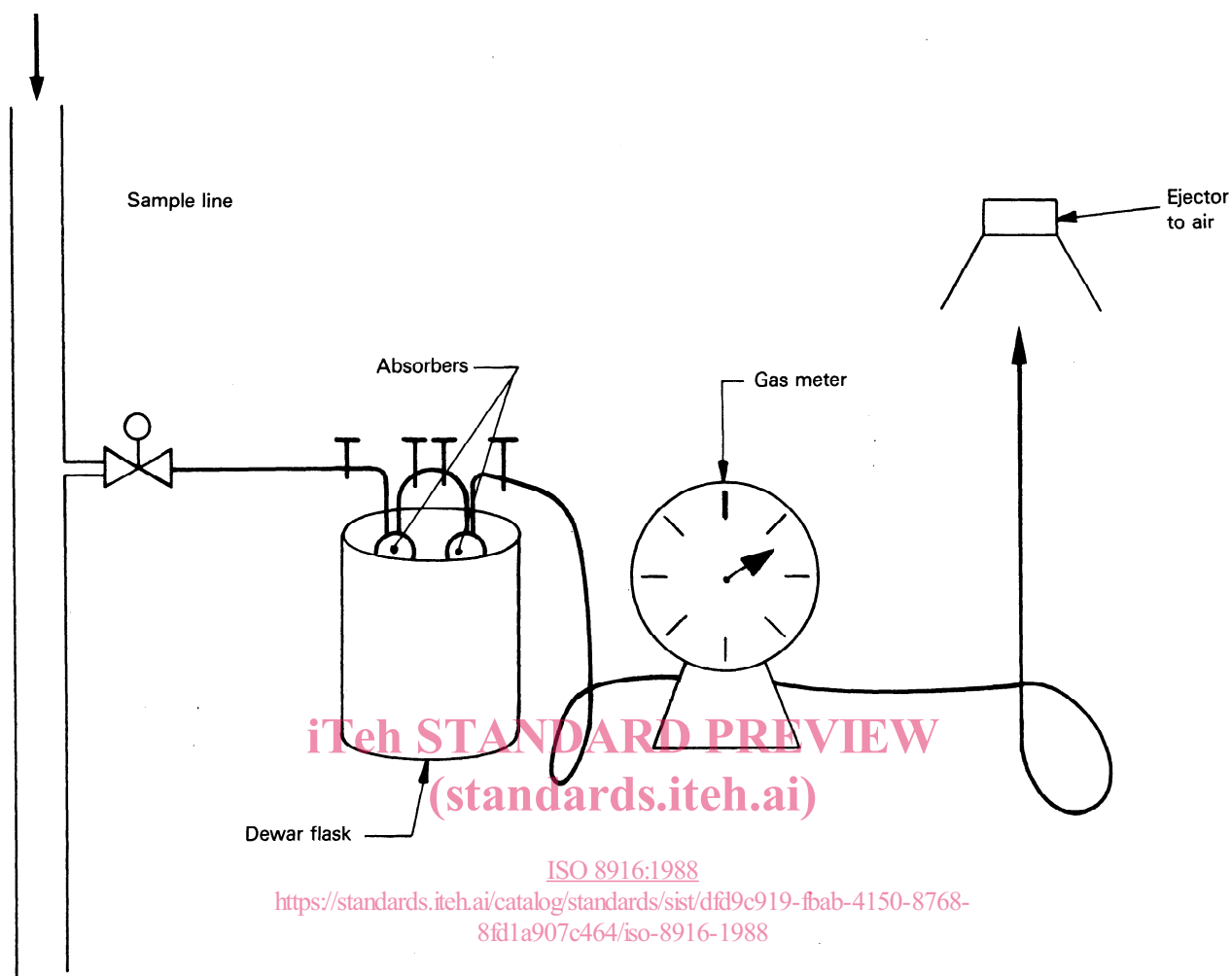


Figure 2 – Schematic representation of apparatus assembly

Annex A (informative)

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ISO 8917 : 1988, *Light olefins for industrial use — Determination of water — Guidelines for use of in-line analysers.*